

Comments from D. Mellard, ATSDR
Draft Data Report for the Vasquez Boulevard & I-70 Residential Soils
Supplemental Investigation: Physico-Chemical Characterization of Soils
Denver, CO

December 2, 1998

1. The statement under 2.1, last paragraph "This means that there is little difference in concentrations in any of the four chemicals for bulk versus fines" may be true for the higher concentrations of arsenic but not true for arsenic concentrations around 400 ppm, the removal action level.

At an XRF bulk sample concentration of 400 ppm arsenic, the corresponding concentration of arsenic in the XRF fine sample is 503 ppm. This is a significant difference when it comes to deciding whether or not a property requires immediate action to stop exposure. If one considers that the removal action level was set for 400 ppm arsenic, the concentration of arsenic in the XRF bulk sample should be 311 ppm when the concentration of arsenic in the XRF fines sample is set at 400 ppm.

$$Y = 1.1685x + 35.697$$

where y is the XRF measurement for fines and x is the XRF measurement for bulk samples

$$400 = 1.1685x + 35.697$$

$$x = 311 \text{ ppm}$$

$$\text{XRF bulk} = 311 \text{ ppm}$$

Therefore, EPA should reconsider the homes where the average concentration of arsenic falls between 311 ppm and 400 ppm for XRF bulk measurements to decide whether or not they should be placed on the list of properties to be remediated under EPA's removal program.

2. The following sentence in the same paragraph does not seem consistent with the data presented in the table under 2.1. Specifically, the text states that the intercept for zinc (i.e., 18) is significantly greater than zero and that the intercept for arsenic (i.e., 36) is nearly significant. It seems that the opposite is more logical based on the numbers.
3. In the same paragraph, consider using another term rather than "small negative bias." It's a difficult concept to understand. My next point is to consider whether or not it's an important concept to discuss since in the case of lead, cadmium, and zinc it does not affect the comparison of bulk and fine samples. It may be an issue to discuss for arsenic but the text already explains the significance of the slope in comparing the two samples. Maybe the issue is the inherent ability of the XRF to measure arsenic in large particles versus arsenic in small particles. But again, the text already addresses that issue by looking at the slope formula itself.

4. I would like to see the calibration curve for arsenic to determine the range of arsenic concentrations where the curve is linear. Concentrations of arsenic outside the linear range should not be part of determining the slope of the fines versus bulk comparison. That may be the reason that the intercept is not zero. Of course, another reason might be the ability of the XRF to measure arsenic in different size particles. Also, the 5 times rule should be applied to the MDL and measurements between the MDL and 5 times the MDL should not be part of the determination of the slope because those measurements are estimated values. In looking at Figure 1A, the correlation of arsenic in fines and bulk seems to have a greater variability at the higher levels of arsenic than at the lower levels. This greater variability seems to start around 800 to 900 ppm. If that's so, that the curve is not linear above, for instance 800 ppm, then those higher levels are affecting the slope and hence the decision about the relationship between the two sample types and whether or not 311 ppm bulk is an appropriate removal action level. Another way to make sure that measurements at either end of the distribution are not affecting the slope of the curve in the middle (for instance at 400 ppm) is to determine the slope in this case for measurements between say 150 ppm and 600 ppm. If the slope is the same then measurements at either end of the curve are not affecting the relationship. If the slope is significantly different then it's a clue to evaluate measurements at both ends of the distribution to determine whether or not they are valid and whether or not they should remain in determining the slope.
5. Figure 2A. Consider renaming "Mass of arsenic in each phase (ppm)" to concentration of arsenic in each chemical form (or something to that effect.) I'm concerned that the phrase "mass of arsenic in each phase" is not understandable to most people.
6. The statement in the paragraph on Quality Control Issues (page 3) about the correlation of 0.95 indicating that there is little difference between the bulk and fine fraction is not the correct interpretation for a correlation coefficient. The high degree of correlation shows that over the range of measurements, the concentrations are highly correlated. That correlation could be that the concentrations are 1:1, 2:1 or 10:1. It is the slope that must be evaluated to determine whether or not there is little difference between the two types of samples.
7. The same paragraph makes a statement that the lower concentration of arsenic using ICP may have resulted from insufficient acid digestion of the soil matrix. More discussion is needed by the technical members of the workgroup to determine which measurement (ICP or XRF) provides the more reliable result. This becomes important in deciding which yards require immediate actions to stop exposure and which concentrations should be used to evaluate long-term exposure.
8. Under Quality Control Samples, 2.1, the text states that the 30% difference between ICP and XRF measurement is not significant. This conclusion is incorrect. The difference may or may not be significant depending upon which analytical method gives the most reliable measurements. It's not known at this time whether or not the difference is large enough to affect the public health significance of long-term exposure to arsenic in soil because that

evaluation has not been conducted yet.

9. Here's the justification for why the 30% difference may or may not be significant.

A. If one assumes that the ICP measurement is more reliable, then one must consider the slopes generated for the ICP measurements and for the XRF measurements.

Here's the logic for what needs to be considered when testing whether or not the action level is appropriate because of the method used in analyzing the concentration of arsenic in soil. (This does not address whether or not 400 ppm arsenic is the appropriate removal action level but rather how the slopes affect using 400 ppm.)

Using 400 ppm arsenic as the removal action level, and assuming that ICP measurements are more reliable than XRF measurements, the following conversions are needed to determine the effect of measurement inaccuracies:

As ICP fines \Rightarrow As XRF fines \Rightarrow As XRF bulk

Therefore,

400 ppm As ICP fines $\Rightarrow y = 0.7286x - 27.073 \Rightarrow y = 1.1685x + 35.697$

$$\begin{array}{lcl} 400 = 0.7286x - 27.073 & \text{and} & 586.2 = 1.1685x + 35.697 \\ x = 586 \text{ ppm} & & x = 471 \text{ ppm} \end{array}$$

400 ppm As ICP fines = 586 ppm As XRF fines = 471 ppm As XRF bulk.

The above logic means that the 400 ppm As in the bulk samples as a removal action level remains protective of public health or that EPA could raise the removal action level to 471 ppm.

I have not done the calculations for lead based on the previous procedure. Should the working group decide that the previous procedure is valid, the action level for lead should be reevaluated. It should go up somewhat because of the slope of $0.7126 + 6$ for ICP fines and XRF fines. The slope for XRF fines and XRF bulk will not affect the conversion significantly.

Now for the other case.

B. If one assumes that XRF measurements are more reliable, then the only factor that affects using the 400 ppm arsenic as the removal action level is the previously discussed difference in the XRF measurements of bulk samples and fines samples. In this case, XRF bulk \Rightarrow XRF fines, and when XRF fines = 400 ppm then XRF bulk = 311 ppm.

For lead, the concentration of lead does not change significantly between XRF fines and XRF bulk samples.

10. The technical people on the VBI70 work group should talk about how to use these slope factors and review the logic described previously. They should also discuss the public health significance of the slope for the comparison of XRF measurements of bulk and fines samples and the public health significance of the slope for the comparison of ICP and XRF measurements for the bulk samples, both as it relates to removal activity and future risk assessments for long-term exposure.
11. Please specify in 2.2 Speciation whether the bulk sample or the fines sample was analyzed.
12. Please specify in 2.3 Particle Size Distribution whether the bulk sample or the fines sample was analyzed.
13. In Figure 4A, it's unclear why there is a fraction at >250 um. If the fines sample was used, there should not be particle sizes greater than 250 um. If the bulk sample was used, then the percent of As in the >250 um should be larger, although less than 50%.
14. Please specify in 2.4 In Vitro Bioaccessibility whether the bulk sample or the fines sample was analyzed.
15. At this time, I have no comments on the in vitro bioaccessibility measurements. I will have to investigate this issue further and decide at a later date its applicability to the risk assessment methods ATSDR will use.